

METHOD FOR SYNTHESIZING OPTICAL QUARTZ GLASS

A. I. Puzynin¹

Translated from *Steklo i Keramika*, No. 9, pp. 29 – 33, September, 2011.

A method for producing optical quartz glass by synthesizing monodisperse silica particles and centrifuging the particles followed by supercritical drying and sintering of porous material is described. The optical transmission spectrum of the optical quartz glass produced by this method is compared with the spectra of several glasses obtained by commercial methods. The advantages of this method over methods based on silicon dioxide aerogels and xerogels for producing quartz glass are indicated.

Key words: optical quartz glass, synthesis, optical transmission spectrum, supercritical technologies.

In industry optical quartz glass (OQG) is made by the gas-flame method. The initial material is rock crystal or synthetic quartz crystals from which, after crushing and acid treatment, 0.1 – 0.4 mm crumb containing at least 99.88 wt.% SiO₂ is obtained. The heat source is a flame from a hydrogen-oxygen burner [1]. Many attempts have been made to develop alternative methods for synthesizing optical quartz glass. In particular, the production of quartz glass by sintering xero- and aerogels has been studied.

An advantage of the xerogels method for obtaining quartz glass [2, 3] is that glass samples of virtually any size and shape can be produced. Xerogels are produced by using the methods of sol-gel chemistry. As a result of polymerization of silicic acid Si(OH)₄, sols of silica SiO₂ particles are formed in an acid medium and then undergo aggregation, forming spatial structure from particles bound to one another (hydrogels or alcogels). These gels are dried at atmospheric pressure, which is why xerogels are obtained.

Next, the xerogels are placed in a muffle furnace and sintered into quartz glass. However, this method has serious drawbacks. The capillary pressure of the liquid in the pores of the gel creates spatial stresses inside the samples, as a result of which cracks form during rapid drying. To avoid cracking the drying time must be increased to several or more weeks, depending on the sizes of the samples, i.e., the full cycle time of the technological process must be increased. In addition, when the sample are dried in open air the shape of the samples becomes distorted, even before sintering in a furnace, making mold calculations difficult.

The aerogel method of obtaining quartz glass [4, 5] makes it possible to decrease substantially the full cycle time

of the production process. In this case, alcogels are dried in autoclaves with parameters (temperature, pressure) above the critical values for the alcohol used, methanol or ethanol. At the transition through the critical point the surface tension and capillary pressure of the liquid in the pores of the gel become zero. All liquid in the entire volume of the autoclave, including the pores of the alcogel, simultaneously transforms into vapor, which is removed from the autoclave, lowering the pressure to the atmospheric value, with constant temperature above the critical value. Because there is no capillary pressure in the pores of the gel, no spatial stresses arise inside the sample during the supercritical drying process. The samples have virtually the same shape as the initial casting; the shrinkage occurring along the linear dimensions during the supercritical drying process is about 4%. Next, the aerogels dried in this manner are sintered in muffle furnaces at temperature about 1100 °C, obtaining defect-free parts from optical quartz glass. The full cycle time is about five days, which is much faster than for the quartz glass production from xerogels.

However, this method has its own drawbacks. The maximum density of the aerogels obtained is about 0.25 g/cm³; the quartz glass density is 2.19 g/cm³. This means that strong linear shrinkage of the aerogel samples occurs during sintering in a muffle furnace. This shrinkage inevitably distorts the initial shape of the samples, and cracks appear in the samples if the drying process is too fast. Heating to 1100°C must be done very slowly (in about 20 h). In addition, because the porosity of aerogels is high, which dictates their low density, a substantial part of the internal volume of the autoclaves is actually occupied only by the alcohol filling the pores of the aerogel. The low density of aerogels decreases the cost-effectiveness of this method (the ratio of the mass of

¹ Federal State Unitary Enterprise "Scientific-Research Institute of Applied Acoustics," Center for High Technologies, Dubna, Moscow Oblast, Russia (e-mail: synop@yandex.ru).

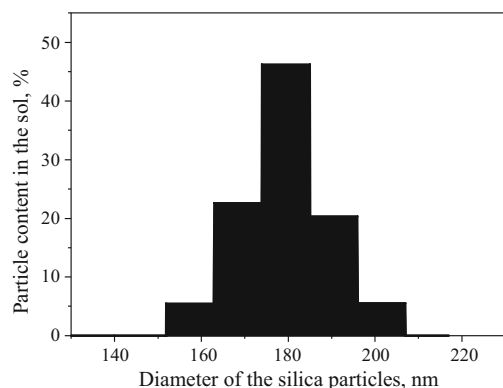


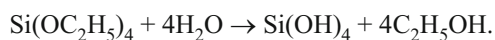
Fig. 1. Characteristic diameter distribution of the spherical silica particles in a sol, the average diameter of the particles is about 180 nm (the measurements were performed with a Nanotracs 253 Ultra laser particle-size analyzer).

the quartz glass parts obtained to the electricity consumption for heating the autoclave and muffle furnace).

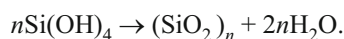
EXPERIMENTAL PART

The present author is proposing a method for producing quartz glass that incorporates the advantages of the “aerogel” technology — relatively short production time — and increases production efficiency at the same time. This method also uses supercritical drying in an autoclave but the samples being dried are produced not by gel formation of a sol of small (about 4 nm in diameter) silica particles in molds, as in aerogel production, but rather by centrifuging large (300 – 400 nm) monodisperse silica SiO_2 particles.

Monodisperse spherical silica particles are formed as a result of the hydrolysis of tetraethoxysilane (TEOS) $\text{Si}(\text{OC}_2\text{H}_5)_4$ in ethyl alcohol with ammonia catalyzing the reaction [6]:



The silicic acid polymerization reaction occurs almost immediately:



The reactions can be controlled by varying the amount of ammonia, temperature, and concentration of the reagents, changing the average diameter of the particles from 30 nm to 1 μm (Fig. 1).

Next, the particle sols synthesized in this manner are centrifuged. In the process a precipitate consisting of a mass of close-packed silica spheres precipitates onto the bottom of the centrifuge vessels (Fig. 2). The precipitate can be transparent, iridescent, or chalk-like, depending on the silica particle sizes and their degree of monodispersity. According to its physical properties the precipitate is a viscous pulp that sticks tightly to the bottom of the centrifuge vessels and in its

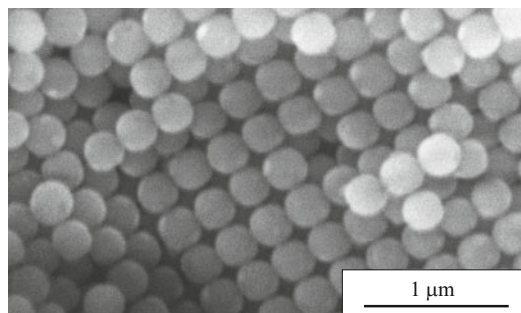


Fig. 2. Electron-microscope photograph of precipitate obtained by centrifuging a sol of spherical monodisperse silica SiO_2 particles (the photograph was taken in a Hitachi S-2600N electron microscope).

raw form cannot be extracted from them without completely destroying it.

Experiments were performed to dry the centrifuged material in air at atmospheric pressure. However, even for very long drying times (more than one month) cracks still appeared in the samples. Defect-free drying of the centrifuged material under normal conditions was found to be impossible, in contrast to drying alcogels into xerogels for subsequent sintering into quartz glass. This effect is explained by the fact that aggregation of silica sols into alcogels is conducted in acidic media. In an acidic medium siloxane bonds Si-O-Si arise between the nearest silica particles at their contact sites. Alcogels, which are three-dimensional structures of silica particles bound to one another, possess adequate strength and at the same time are elastic under strain. Alcolgel particles continue to shrink until the capillary pressure of the liquid in pores is balanced by the mechanical strength of the gel structure as described by the Laplace equation:

$$p = \frac{2\sigma}{r} \cos \theta,$$

where p is the capillary pressure of the pore liquid, σ is the interphase surface tension, r is the capillary radius, and θ is the wetting angle.

For synthesis of monodisperse silica particles, the reaction proceeds in an alkaline medium ($\text{pH} = 8 - 9$). Because hydroxide ions OH^- are adsorbed from the solution, the surfaces of the particles carry like charges. The repulsion forces between charges hamper the coagulation of the particles, and stable sols form owing to these forces. The same repulsion forces are responsible for the fact that the structure of centrifuged material is much weaker than that of alcogels. As it dries under normal conditions this material undergoes bulk deformation under the capillary forces — capillary contraction and internal stresses appear, as a result of which cracks form. Because there are no chemical bonds between neighboring particles the centrifuged material is inelastic and incapable of withstanding deformation without breaking down.

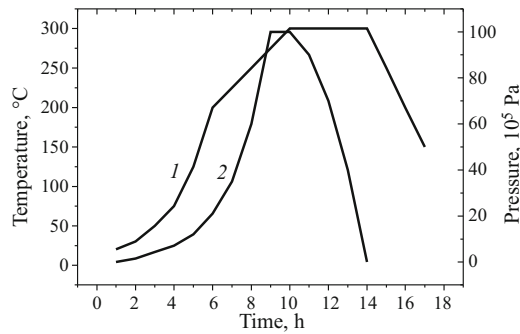


Fig. 3. Plots of the temperature (1) and pressure (2) variations in an autoclave during supercritical drying.

The present author used the method of supercritical drying to achieve defect-free drying of the centrifuged material.

A one-liter stainless steel autoclave with inner diameter 105 mm was used for supercritical drying. After centrifuging, to remove excess ammonia from the centrifuge vessels the liquid in which the silica particles were synthesized (ethanol with ammonia) was poured out and replaced with pure ethanol. Next, the vessels were placed inside an autoclave, which was filled with 0.5 liters ethanol, hermetically sealed, blown with nitrogen, and heated. The temperature in the autoclave was raised evenly, because if heating is rapid there will not be enough time for the expanding alcohol to exit through the pores of the sedimented material, which can cause defects to appear in it. The thinner the sample, the more rapidly it can be heated. The critical parameters for ethanol are: $T_{cr} = 516$ K, $p_{cr} = 6.4$ MPa. But it also contains about 4% water ($T_{cr} = 647.3$ K, $p_{cr} = 22.12$ MPa). For this reason, to create a reserve the autoclave was heated to 300°C and the pressure in it was maintained constant at approximately 9.5 MPa. At the moment the critical point is crossed the ethanol in the entire volume of the autoclave, including in the pores of the material, transforms into vapor, and the surface tension and capillary pressure of the liquid in the pores drop to zero, all occurring simultaneously. Next, at constant temperature 300°C the ethanol vapor was continually released from the autoclave, and in the process the pressure dropped from 9.5 MPa to atmospheric pressure. The critical values of the density for ethanol and water vapors are quite high — $\rho_{cr} = 0.276$ g/cm³ and $\rho_{cr} = 0.32$ g/cm³, respectively. Defects can also appear in the sample if pressure is shed too rapidly. For this reason, a shedding regime in which the pressure was reduced at a rate inversely proportional to the instantaneous pressure was chosen:

$$\frac{dp}{dt} \sim -\frac{1}{p}.$$

In such a regime the rate of pressure shedding is small initially, when the pressure in the autoclave is high, but it increases as pressure decreases. The temperature was raised and pressure lowered in regimes which the present author optimized in the course of the production of silicon dioxide

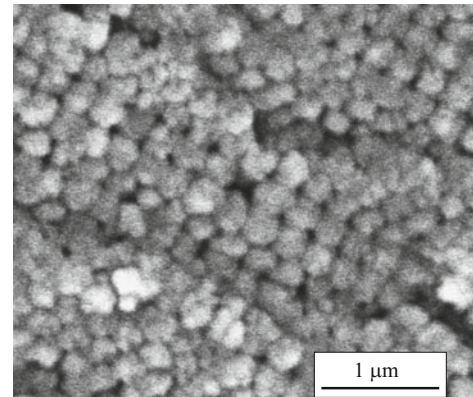
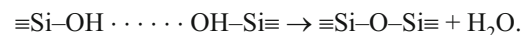


Fig. 4. Structure of material sintered at 1150°C, sintering time 4 h (the photograph was made in a JEOL JSM-840 scanning electron microscope).

aerogel [7]. After the pressure was lowered to the atmospheric value nitrogen was blown through the autoclave at constant temperature in order to remove residual ethanol vapors from it. These vapors condense on cooling, which also can damage the samples. The heating of the autoclave was switched off after the nitrogen was blown through (Fig. 3).

During supercritical drying the samples of porous material shrink by approximately 2% in diameter, which makes it possible to extract them easily from the centrifuge vessels. The strength of the samples during supercritical drying increased considerably, since at high temperature partial condensation of the OH groups occurs on the surface of the silica spheres, which results in the formation of common siloxane bonds between neighboring silica particles [8]:



After drying, the samples are placed in a muffle furnace to be sintered.

The melting temperature $T_m(r)$ of a small spherical particle with radius r is calculated using the Thompson relation

$$T_m(r) = T_m \left(1 - \frac{2\sigma v}{Lr} \right),$$

where T_m and L are the melting temperature and specific heat of a massive solid body, σ is the specific surface energy of the solid particle – melt interface, and v is the specific volume [9].

This dependence of the melting temperature on particle size shows that materials consisting of nanosize silica particles can be sinter into glass at temperatures which are much lower than the temperature (1700°C or higher) required to melt quartz crumb in the industrial production of quartz glass.

As the temperature in the muffle furnace is raised evenly (the optimal rate of heating about 150 K/h), the samples begin to sinter uniformly above 1000°C. The silica particles gradually melt (Fig. 4), and the sizes of the pores between

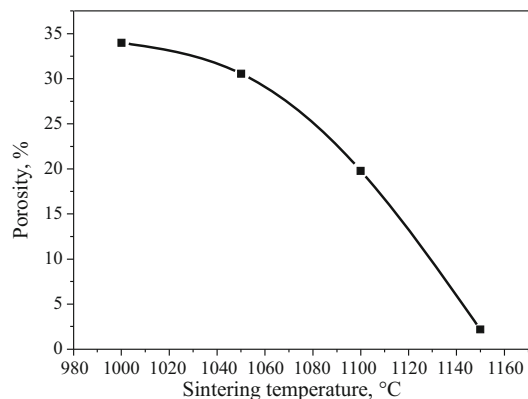


Fig. 5. Material porosity versus sintering temperature (the average diameter of the silica spheres is about 320 nm, the sintering time at each temperature is 4 h).

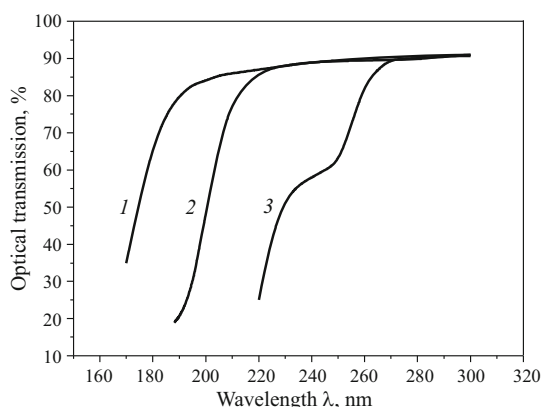


Fig. 6. UV-range optical transmission spectra: 1) KI grade optical quartz glass; 2) quartz glass produced by the technology described; 3) KV grade optical quartz glass; sample thickness 10 mm, reflection losses included.

them and correspondingly the total porosity of the entire material decrease (Fig. 5). Samples consisting of silica spheres with average diameter about 320 nm underwent final sintering into quartz glass with a temperature reserve of about 1200°C. In “aerogel” technology the final sintering is conducted at temperature near 1100°C, since the silica particles forming the aerogel structure are 4–5 nm in size [10].

The complete synthesis cycle for OQG produced by this method is no longer than five days.

OPTICAL TRANSMISSION SPECTRUM OF SYNTHESIZED QUARTZ GLASS

The optical transmission spectrum of this quartz glass was compared with that of some other Russian optical quartz glasses obtained by industrial methods (Fig. 6). This comparison of the spectra in combination with the chemical composition of the glass, determined by its synthesis conditions,

made it possible to categorize the quartz glass synthesized by the present author as an optical quartz glass.

By using polytetrafluoroethylene (Teflon) vessels instead of glass vessels in the centrifuge and conducting supercritical drying in a Teflon-lined autoclave the present author plans to improve the optical properties of the quartz glass which he synthesizes. The liquids in the supercritical state are extremely good solvents. For example, supercritical ethanol easily dissolves some inorganic salts. During a relatively prolonged supercritical drying process various impurities can dissolve in ethanol, migrating into it from the walls of the autoclave and centrifuge vessels, and then diffuse into the porous samples and become adsorbed on the surfaces of the silica spheres. After sintering in a furnace these impurities remain inside the OQG, which probably degrades the optical properties of the glass somewhat. Teflon centrifuge vessels as well as a lined autoclave can help avoid this.

CONCLUSIONS

The synthesis method described above makes it possible to produce parts from optical quartz glass using laboratory equipment — thermostat, centrifuges, autoclave, and muffle furnace with maximum heating temperature not higher than 1250°C. The linear dimensions of the OQG samples will be limited by the diameters of the centrifuge vessels and autoclave.

Supercritical drying in an autoclave is a technological bottleneck for these technologies. This is the most energy intensive process, the autoclave claiming most of the equipment costs. As indicated above, the maximum density of aerogels is about 0.25 g/cm³. The density of the porous material obtained by centrifuging spherical monodisperse silica particles is 1.4 g/cm³. This means that in this production method the autoclave will be used approximately five times more efficiently relative to the mass of the samples dried in it. The linear shrinkage of the samples obtained by means of centrifuging is about 14% after they are sintered in a furnace and the shrinkage of aerogel samples is about 50%, i.e., in the first case it is easier to make a part whose dimensions are close to the prescribed shape.

Compared with OQG production by sintering xerogels, the method described here has advantages because of its much shorter production cycle time as well as smaller linear shrinkage of the final article relative to the initial dimensions.

The following comments can be made concerning the possible application of porous silica materials produced with this technology. After sintering in a furnace at temperature about 1000°C the material acquires adequate strength (Vickers hardness about 100 [11]) while retaining high open porosity (about 33%). The monodisperse silica spheres are close-packed (see Fig. 2). For this reason the pores between the spheres also have the same dimensions, and they can be varied by changing the diameters of the synthesized silica

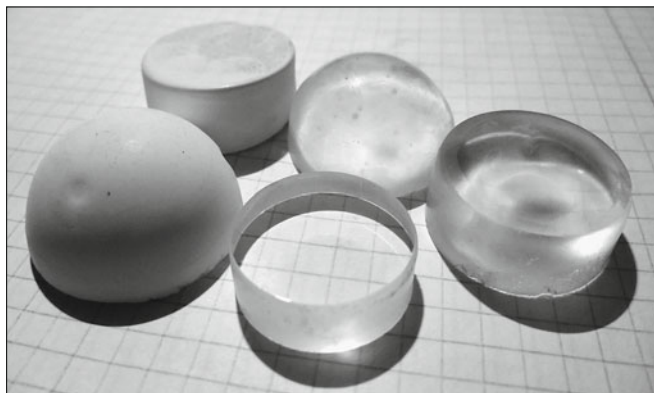


Fig. 7. Two porous samples sintered in a muffle furnace at temperature 1000°C (left-hand side) and three samples sintered at 1200°C into quartz glass. One of the quartz glass samples was ground and polished.

spheres. These porous materials (Fig. 7) can be used as filters with a narrow pore-size distribution and carriers for catalysts in acidic and neutral media as well as in chromatography.

REFERENCES

1. M. L. Sulimenko, *General Technology of Silicates* [in Russian], Moscow (2004).
2. E. M. Rabinovich, D. W. Johnson, J. Mac. Chesney, and E. V. Vogel, "Preparation of high-silica glasses from colloidal gels: I. Preparation for sintering and properties of sintered glasses," *J. Am. Ceram. Soc.*, **66**, 683 (1983).
3. G. W. Scherer and J. C. Luong, "Glasses from colloids," *J. Non-Cryst. Solids*, **63**, 163 (1984).
4. J. Phalippou, T. Woignier, and M. Prassas, "Glasses from aerogels. Pt. 1. The synthesis of monolithic silica aerogels," *J. Mater. Sci.*, **25**, 3111 (1990).
5. T. Woignier, J. Phalippou, and M. Prassas, "Glasses from aerogels. Pt. 2. The aerogel-glass transformation," *J. Mater. Sci.*, **25**, 3118 (1990).
6. W. Stober, A. Fink, and E. Bohn, "Controlled growth of monodisperse silica spheres in the micron size range," *J. Colloid Interface Sci.*, **26**, 62 – 69 (1968).
7. Yu. K. Akimov, V. P. Zrelov, A. S. Moiseenko, et al., "Fabrication of large-size silicon dioxide aerogel samples in a 37-liter autoclave and investigation of the aerogel optical properties," *Pis'ma Zh. Fiz. Elementar. Chastits Atom. Yadra*, No. 1, 48 – 57 (2000).
8. A. I. Puzynin and S. V. Filin, "Application of supercritical drying during synthesis of precious opals," *Physics of Crystallization* [in Russian], TGU, Tver' (1999), pp. 89 – 96.
9. A. A. Barybin and V. I. Shapovalov, "Differential control for melting temperature of small particles," *Pis'ma Zh. Tekh. Fiz.*, **36**(22), 69 – 75 (2010).
10. S. Henning and L. Svensson, "Production of silica aerogel," *Phys. Scripta*, **23**, 697 – 702 (1981).
11. S. V. Filin, A. I. Puzynin, and V. N. Samoilov, "Some aspects of precious opal synthesis," *Australian Gemmologist*, **21**, 278 – 282 (2002).